

Systematic enumeration of crystalline networks with only sp^2 configuration in cubic lattices

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Systematic enumeration of crystalline networks with some special topological characters is of considerable interest in both mathematics and crystallography. Based on the restriction of lattice in cubic and inequivalent nodes not exceeding three, a simple method is proposed for systematic searching for three-dimensional crystalline networks with only sp^2 -configuration nodes (C- sp^2 -TDTCNs). We systematically scan the cubic space groups from No.195 to No.230 and find many C- sp^2 -TDTCNs including all the previously proposed cubic ones. These C- sp^2 -TDTCNs are topologically intriguing and can be considered as good templates for searching carbon crystals with novel properties, predicting high pressure phases of element nitrogen and designing three-dimensional hydrocarbon crystals. Structure optimizations are considered by regrading these C- sp^2 -TDTCNs as carbon crystals and the corresponding energetic stability of these carbon crystals are evaluated, using the density functional theory (DFT) based first-principle calculations. Our results are of wide interests in mathematics, condensed physics, crystallography and material science.

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INTRODUCTION

Systematic enumeration of crystalline networks with some special topological characters is of considerable interest in both mathematics and crystallography. With particular importance, the three-dimensional (TD) four- and/or three-connected networks relevant to a wide range of systems (especially to the crystal structures, such as zeolitic and the well-known diamond) have been systematically investigated [1–11]. TD three-connected networks (TDTCNs) have also been considered [2, 4, 6, 8] as topologically intriguing structures in mathematics and are also significant in crystallography. The crystalline ground state of carbon, namely graphite, contains carbon atoms with perfect sp^2 -configuration (the ground state of the binary compound of boron and nitrogen, hexagonal boron nitride, also prefers such a sp^2 -configuration). But the graphite structure is not an exact TD network. Many efforts have been paid on predicting carbon crystals with sp^2 -configuration in exact TD networks with the belief that graphite is not the only way to fill the TD space with only trigonal sp^2 -like atoms [12–39]. There are many TDTCNs [2, 4, 6, 8] satisfying such a requirement and some of them have been investigated as carbon crystals [12–39] showing novel physical properties. The second fact implying the signification of TDTCNs (especially of those with sp^2 -configuration, sp^2 -TDTCNs) is about nitrogen. At ambient condition, element nitrogen forms the only gas phase of molecular N_2 with nitrogen-nitrogen triple bond. With the progress in high pressure technology, scientists realized a phase transition from molecular nitrogen (N_2) to an incompressible

single-bonded cubic gauche phase (cg- N) [40, 41]. In such a novel solid phase, nitrogen atoms form nontraditional sp^3 -hybridization where three electrons bond to three neighbours (fill three sp^3 -hybridized orbits) forming a distorted sp^2 -configuration and the lone pair electrons fill the fourth sp^3 -hybridized orbit. Many followed theoretical predictions [42–47] also show that high pressure nitrogen prefers the TDTCNs with distorted sp^2 -configurations. Thirdly, sp^2 -TDTCNs are also good templates for designing TD hydrocarbon crystals. Many efforts have been paid in this direction [48–53]. For example, K4-carbon [35–37] to K4-hydrocarbon [53], graphene [54] to graphane [48] and graphite to graphane crystals [49].

Predictions of the TDTCNs can be found in many previous works [2, 4, 6, 8] and the predictions of non-graphite TD sp^2 -hybridized carbon crystals, according to our knowledge, were started in 1983 by Hoffmann (bct4-carbon) [12]. Since 1983, many scientists have reported their predictions on TD sp^2 -hybridized carbon crystals, such as H6-carbon in 1990 [13], 6.8²D (polybenzene) and 6.8²P in 1992 [24], 6.8²G and P56 in 1993 [25], carbon forms in 1995 [26], C20-carbon in 1997 [27] and later in 1998 [28], FCC-(C₂₈)₂, FCC-(C₃₆)₂ and FCC-(C₄₀)₂ in 1998 [23], R6-carbon and BCT8-carbon in 1998 [29], FCC-(C₆₄)₂ in 2003 [32], K4-carbon in 2008 [35] and 2009 [36, 37], C₁₅₂ and C₂₀₀ in 2010 [21], TD tubular carbons [14, 33, 34, 38, 39] and Schwarzite carbons (P, D, G surface) [15–21, 25]. By combining graph theory with quantum mechanics, Winkler et al. systematically predicted [30, 31] 14 TD sp^2 -hybridized carbon crystals with up to six atoms per unit cell. Their

results include previously proposed bct4-carbon[12], H6-carbon[13], R6-carbon[29] and K4-carbon[35–37]. Very recently, with the idea of substitution mentioned by Sheng et al (T-carbon)[55], we have also successfully constructed[56] a simple TD sp²-hybridized carbon crystal (sp²-diamond) with intriguing configuration, which belongs to the same space group of diamond and has only one inequivalent atomic position. However, the number of the TDTCNs is infinite. We can not enumerate all of them without any restrictions. In this paper, we report a partial solution to this problem, based on a restriction of lattice in cubic and inequivalent atomic positions not exceeding three. With such a restriction and the group theory, a systematic (not a global) enumeration of cubic TDTCNs with sp²-like topological configurations (C-sp²-TDTCNs) by designed-computational-program becomes possible. We have systematically scanned all the cubic space groups from No.195 to No.230 and found many C-sp²-TDTCNs including all the previously proposed cubic ones.

METHOD

Before we introduce the method of our systematic enumeration of C-sp²-TDTCNs, four simple but very useful rules are discussed. **Rule one**, if a C-TDTCN contains only one inequivalent atomic position, the three neighbours for every atoms are themselves; **Rule two**, if a C-TDTCN contains only two inequivalent atomic positions, its two inequivalent atoms form a chemical bond. **Rule three**, if a C-TDTCN contains only three inequivalent atomic positions, its three inequivalent atoms form an angle. **Rule four**, variation of lattice constant for any cubic crystal does not affect its bond angles. Based on these four simple rules, we can systematically search C-sp²-TDTCNs with one, two and three inequivalent atoms by random putting an atom, a bond and an angle, respectively, in a given cubic lattice in a special space group with a defined sp²-criterion. Such an idea enhances the probability of generating C-sp²-TDTCNs in comparison with a totally random method. A simple procedure implementing such an idea is shown in Fig1. Predictions of C-sp²-TDTCNs containing more than three inequivalent atomic positions or belonging to non-cubic lattice become more complicated (that can also be solved in principle) and are not considered in our present work.

Based on the procedure shown Fig1, one can systematically search C-sp²-TDTCNs in the following four simple steps. I), Choose a cubic lattice with designated lattice constant and space group and set a sp²-criterion for identifying structures as C-sp²-TDTCNs, namely the cutoff radius (R_{cut}) for the fourth neighbour, the minima and maxima of bond lengths (R_{min} , R_{max}) and bond angles (θ_{min} , θ_{max}) in C-sp²-TDTCNs.

Choose a cubic space group and set the criterion for identifying structures as C-sp ² -TDTCN [R_{cut} , (θ_{min}^s , θ_{max}^s) & (R_{min}^s , R_{max}^s)]
Index A: Input random position or positions for inequivalent atom or bond or angle
Initial structure constructing: Operate the inputted position or positions to create a structure and record all the atomic positions in the cubic lattice
Rationality evaluation if it is a TDTCN (R_{cut}) Calculate the bond angles and length for each inequivalent atoms and find out the θ_{min}^s , θ_{max}^s , R_{min}^s and R_{max}^s in this structure. If $\theta_{min}^s < \theta_{min}$ or $\theta_{max}^s > \theta_{max}$, give up and go to A to create a new structure If $R_{min}^s < R_{min}$ and $R_{max}^s > R_{max}$, give up and go to A to create a new structure If $R_{min}^s < R_{min}$ and $R_{max}^s < R_{max}$ If $R_{max}^s * R_{min} / R_{min}^s > R_{max}$, give up and go to A to create a new structure If $R_{max}^s * R_{min} / R_{min}^s < R_{max}$, record and enlarge the cell with ratio of R_{min} / R_{min}^s . If $R_{min}^s > R_{min}$ and $R_{max}^s > R_{max}$ If $R_{min}^s * R_{max} / R_{max}^s < R_{min}$, give up and go to A to create a new structure If $R_{min}^s * R_{max} / R_{max}^s < R_{min}$, record and reduce the cell with ratio of R_{max} / R_{max}^s . If $R_{min}^s > R_{min}$ and $R_{max}^s < R_{max}$, record the structure with the initial cell

FIG. 1: Procedure for systematic searching for C-sp²-TDTCNs

II), Randomly input the position or positions for the inequivalent atom or bond or angle in the chosen lattice and operate them by corresponding symmetry operators to construct a testing-crystal. III), Calculate the bond lengths and bond angles for each inequivalent atoms in the created testing-crystal and find out the minima (R_{min}^s , θ_{min}^s) and maxima (R_{max}^s , θ_{max}^s) for bond lengths and bond angles, respectively. IV), Evaluate the rationality of the testing-crystal according to the following five conditions if it can be considered as a three-connected network (The requirement of R_{cut} is satisfied): a) $\theta_{min}^s < \theta_{min}$ or $\theta_{max}^s > \theta_{max}$ indicates that such a structure dose not satisfy the requirements of bond angle. We give up it directly because further cell enlarging or reducing can not change the angles according to the rule four mentioned before. b) $R_{min}^s < R_{min}$ and $R_{max}^s > R_{max}$ indicate that such a structure dose not satisfy both the minimum and maximum requirements of bond length. We give up it directly because further cell enlarging (reducing) can not enlarge (reduce) the R_{min}^s (R_{max}^s) and reduce (enlarge) the R_{max}^s (R_{min}^s), making the requirements of bond length satisfied. c) $R_{min}^s < R_{min}$ and $R_{max}^s < R_{max}$ indicate that such a structure dose not satisfy the minimum bond length requirement. We then enlarge the crystal cell with ratio of R_{min} / R_{min}^s to make the crystal satisfying the minimum bond length requirement. If the structure is still a three-connected one and the maximum bond length requirement is satisfied (namely, $R_{max}^s * R_{min} / R_{min}^s < R_{max}$), we record the enlarged structure (otherwise give it up). d) $R_{min}^s > R_{min}$ and $R_{max}^s > R_{max}$ indicate that such a structure dose not satisfy the maximum bond length requirement. We then reduce the crystal cell with ratio of R_{max} / R_{max}^s to make the crystal satisfy the maximum bond length require-

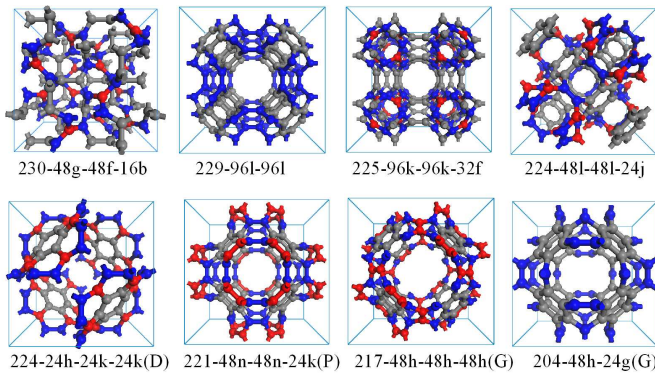


FIG. 2: Some selected crystalline views of new C-sp²-TDTCNs found in present work. Different colors indicate inequivalent atomic positions and D, G, P indicate the surface types.

ment. If the reduced structure is still three-connected one and the minimum bond length requirement is still satisfied (namely, $R_{min}^s \cdot R_{max} / R_{max}^s > R_{min}$), we record the reduced structure (otherwise give it up). e) $R_{min}^s > R_{min}$ and $R_{max}^s < R_{max}$ indicate that such a structure directly satisfies both maximum and minimum bond length requirements and we record it directly.

RESULTS AND DISCUSSION

In our present work we systematically enumerate the C-sp²-TDTCNs by the method as discussed above. We name all the C-sp²-TDTCNs with their space group number and their corresponding Wyckoff positions. For example, the previously proposed 6.8²D[24], C20-carbon [27, 28] and P192 [17](P8[19]), containing one, two and three inequivalent atoms, are named as 224-24i, 225-48h-32f and 229-96l-48k-48k, respectively. With such a nomenclature, we can know the fundamental information of a structure, which are useful for identifying if it has been proposed previously and excluding repeating structures. Based on such a nomenclature, some C-sp²-TDTCNs possess the same name due to their commonness in both space group and Wyckoff positions. We provide their structural characters to distinguish them. We have systematically scanned all the cubic space groups from No.195 to No.230 based on the requirements of cutoff radius of 2.0 Å, bond angles distributing in 109°-135° and bond lengths within the range from 1.3 Å to 1.7 Å and found many structurally intriguing C-sp²-TDTCNs including all the previously proposed cubic ones (some of them are selected to show in Fig2). Especially, C-sp²-TDTCNs can be found in every space group but some of them degenerate to the ones with relatively higher symmetry.

The summarized lattice constants and inequivalent

atomic positions for these C-sp²-TDTCNs are based on the post-processes of structure optimizations by regarding these C-sp²-TDTCNs as sp²-hybridized carbon crystals. We have considered further energy evaluation for these C-sp²-TDTCNs. In the following, we introduce our results of C-sp²-TDTCNs templates for sp²-like carbon crystals, high pressure crystals of element nitrogen and TD hydrocarbon crystals.

C-sp²-TDTCNs with one inequivalent position

In our searching process, only seven C-sp²-TDTCNs containing one inequivalent atomic position were found. Although our searching process is non-global, we still believe that there are only seven C-sp²-TDTCNs with one inequivalent atomic position under the given requirements of cutoff radius, bond lengths and bond angles. We identify that six of them are the previously proposed 6.8²G (No.230)[16, 25], interpenetrated-K4 (No.230, we refer it as IK4)[4, 8], 6.8²P (No.229) [24], sp²-diamond (No.227)[56], 6.8²D (No.224)[24] and K4 (No.214)[35–37] crystals. Their crystalline views (fully optimized carbon crystals with first-principles method with calculation details provided in the supplementary information) are shown in FigS1. (a), (b), (c), (d), (e) and (f), respectively, in the supplementary information. We name these C-sp²-TDTCNs as 230-96h, 230-16b, 229-48k, 227-96g, 224-24i and 214-8a, respectively, according to their space group numbers and Wyckoff positions. Their corresponding lattice constants and inequivalent atomic positions are summarized in Table SI in the supplementary information. The seventh one belonging to 206 space group has not been reported as a carbon crystal before but was proposed as the 3/6/c5 configuration by E. Koch et. al in 1995[6] (The structure of sp²-diamond[56] was also proposed as 3/6/c3 by E. Koch 1995[6]). Its perspective views of both crystalline and primitive cells are shown in FigS1 (g) and (h), respectively. From its crystalline view, we can see that it contains eight interconnected benzene rings in its cubic cell similar to that of 229-48k but in different connecting manner. We name it as 206-48e according to its space group number and the fact that it contains one inequivalent atomic position at the Wyckoff position of 48e (0.888, 0.985, 0.155).

We have also found, in some other space group, many C-sp²-TDTCNs with only one inequivalent atomic position, which degenerate to the seven ones with relatively higher symmetry. For example, we found four equivalents for 224-24i (6.8²D) in space groups 228 (228-192h), 227 (227-192i), 215 (215-24j) and 201 (201-24h), respectively. More equivalent relations among these C-sp²-TDTCNs with only one inequivalent atomic position are shown in Table SI. Furthermore, these seven inequivalent C-sp²-TDTCNs can also be found in the following two con-

TABLE I: The nominations, characters or previous names (Ch/Pn), lattice constant (LC:Å), inequivalent positions (POS), and cohesive energy (Ecoh: eV/atom) of C-sp²-TDTCNs with two inequivalent atomic positions

C-sp ² -TDTCNs	Ch/Pn	LC	POS1	POS2	Ecoh
230-96h-48g	New	10.341	(-0.144,-0.326, 0.776)	(-0.301,-0.875, 0.551)	-6.824
229-96l-96l	New	12.534	(-0.389, 0.231,-0.311)	(0.054,-0.222,-0.629)	-7.278
227-192i-192i	D96-D8	18.048	(0.339,-0.716,-0.606)	(0.811,-0.412,-0.534)	-7.443
227-96g-32e	D32-D8	11.203	(0.834,-0.166, 0.506)	(0.387, 0.613, 0.613)	-7.191[57]
227-192i-96g	D72-D9	15.605	(0.130, 0.431,-0.749)	(-0.281, 0.925,-0.781)	-7.253
226-192j-64g	New	13.227	(0.399,-0.447,-0.796)	(0.621,-0.621,-0.379)	-7.191
225-48h-32f	C20[27, 28]	9.146	(-0.139,-0.139, 0.139)	(0.000,-0.198, 0.198)	-6.878
225-48g-32f	New	9.572	(0.250, 0.430,-0.250)	(0.850, 0.650,-0.650)	-6.819
225-192l-96k	New	15.146	(0.596,-0.839,-0.728)	(0.455,-0.307,-0.307)	-7.219
225-192l-96j	New	14.789	(-0.283, 0.352, 0.418)	(-0.224, 0.500, 0.341)	-7.289
224-48l-48l	D96-D8	9.168	(0.728, 0.837, 0.947)	(0.323, 0.572, 0.876)	-7.316
224-12g-8e	New	5.342	(0.000, 0.000, 0.362)	(0.358, 0.642, 0.642)	-6.721[57]
221-24m-24l	P48-P9	8.197	(0.083, 0.353, 0.353)	(0.500, 0.838, 0.278)	-7.124
221-48n-24l	P72-P8	9.464	(0.840, 0.371, 0.734)	(0.072, 0.500, 0.726)	-7.525
221-48n-24k	P72-P8	9.462	(0.339, 0.234, 0.129)	(0.000, 0.572, 0.774)	-7.521
220-24d-16c	New	6.808	(0.234,-0.500, 0.250)	(-0.412,-0.412, 0.588)	-7.118
217-12e-8c	Cage-N10[47]	4.979	(0.648, 0.000, 0.000)	(0.324,-0.324,-0.324)	-6.249
215-6g-4e	New	4.904	(0.500, 0.500, 0.140)	(0.693, 0.307, 0.307)	-6.365
215-24j-24j	New	8.723	(0.076, 0.458, 0.347)	(0.677, 0.789, 0.561)	-7.188
214-48i-48i	G48-G8	10.532	(0.347,-0.640, 0.196)	(0.007,-0.669, 0.492)	-7.039
212-24e-8c	New	7.705	(0.803, 0.473, 0.305)	(0.715, 0.715, 0.715)	-6.972[57]
205-24d-8c	New	6.391	(0.410, 0.390, 0.672)	(0.258, 0.242, 0.758)	-6.967
204-48h-24g	G36-G7	9.365	(-0.133,-0.342, 0.274)	(0.285, 0.000, 0.572)	-7.517
200-12j-8f	New	5.451	(0.241, 0.369, 0.000)	(0.223, 0.777, 0.777)	-7.067
195-6g-4e	New	4.1303	(0.000, 0.500, 0.322)	(0.241, 0.759, 0.759)	-6.366

ditions of considering about two and three inequivalent atomic positions in a cubic cell. See the details of equivalent relations in all the C-sp²-TDTCNs in Table SII and SIII in the supplementary information.

C-sp²-TDTCNs with two inequivalent positions

When we consider the situation of C-sp²-TDTCNs containing two inequivalent atomic positions, we have found 25 inequivalent C-sp²-TDTCNs. The perspective crystalline views of these 25 inequivalent C-sp²-TDTCNs are shown in FigS2 in the supplementary information and their corresponding lattice constants and inequivalent atomic positions are summarized in Table I. Most of the 25 C-sp²-TDTCNs are new except that the C20-carbon (225-48h-32f) has been proposed as a carbon crystal[27, 28] and the cage-N10 (217-12e-8c) has been proposed [47] as a high pressure nitrogen phase. Some of them can be regarded as new Schwarzite surfaces (indicated in Table I), such as 227-192i-192i (D surface with 96 atomic positions in its primitive cell and octagon rings, D96-D8), 221-24m-24l (P surface with 48 atomic positions in its primitive cell and nonagon rings, P48-P9) and 204-48h-24g (G surface with 36

atomic positions in its primitive cell and heptagon rings, G36-G7). These C-sp²-TDTCNs distribute in space groups of 230, 229, 227, 226, 225, 224, 221, 220, 217, 215, 214, 212, 205, 204, 200, and 195. Some of them can also be found in other space groups or in the following condition of C-sp²-TDTCNs containing three atomic positions (see the equivalent relations in Table SII and SIII in the supplementary information). In addition, we have also found some C-sp²-TDTCNs with two inequivalent atomic positions degenerating to those with only one inequivalent atomic position. Such as the one named as 228-96g-96g is equivalent to 224-24i (6.8²D). More examples can be found in Table SII in the supplementary information.

C-TDTCNs with three inequivalent positions

There are more C-sp²-TDTCNs containing three inequivalent atomic positions and the increase of the inequivalent atomic positions enlarges the state space and reduces the probability of meeting the special C-sp²-TDTCNs in our searching process. Fortunately, we have found 48 of them including some Schwarzite type surface structures (indicated in Table II), such as the G type

TABLE II: Nominations, characters or previous names (Ch/Pn), Lattice constant (LC:Å), Inequivalent positions (POS), Cohesive energy (Ecoh: eV/atom) of C-sp²-TDTCNs with three inequivalent atomic positions

C-sp ² -TDTCNs	Ch/Pn	LC	POS1	POS2	POS2	Ecoh
230-96h-96h-96h	G144-G8	15.944	(-0.054,-0.491, 0.569)	(-0.152,-0.559, 0.661)	(-0.099,-0.488, 0.644)	-7.531
230-48g-48f-16b	New	9.882	(-0.021,-0.375, 0.271)	(0.000,-0.825, 0.451)	(-0.125,-0.375, 0.375)	-7.034
230-96h-96h-48f	New	12.038	(-0.035,-0.342, 0.501)	(-0.134,-0.400, 0.531)	(0.000,-0.250, 0.564)	-7.283
229-96l-48k-16f	New	11.844	(0.229, 0.638, 0.059)	(0.413, 0.263,-0.263)	(0.317, 0.317, 0.317)	-7.125
229-48j-48k-48k	New	11.739	(0.241,-0.156, 0.000)	(0.327,-0.187,-0.187)	(0.281,-0.111,-0.111)	-7.013
229-96l-48k-48k	P192-P8[17, 19]	14.901	(0.278,-0.047, 0.396)	(0.289,-0.173, 0.289)	(0.324,-0.091, 0.324)	-7.627
228-192h-96g-32b	New	14.433	(-0.326, 0.857, 0.542)	(-0.375, 0.698, 0.553)	(-0.375, 0.625, 0.625)	-7.175
227-96g-96g-32e	New	12.652	(0.169,-0.533, 0.830)	(0.068,-0.288, 0.788)	(0.171,-0.171, 0.671)	-7.207
227-96g-96g-96g	FCC-(C ₃₆) ₂ [23]	17.491	(-0.105, 0.605, 0.801)	(-0.244, 0.858, 0.858)	(-0.123, 0.778, 0.778)	-7.125
227-192i-192i-96g	D120-D7	18.994	(-0.402,-0.711,-0.005)	(-0.910,-0.804, 0.357)	(-0.725,-0.275,-0.030)	-7.518
227-192i-96g-32e	FCC-(C ₄₀) ₂ [23]	15.881	(-0.083,-0.021, 0.703)	(0.063,-0.326, 0.937)	(0.108,-0.392, 0.892)	-7.324
227-192i-192i-192i	D144-D8	23.623	(-0.315, 0.273,-0.358)	(-0.225, 0.317,-0.397)	(-0.416, 0.209,-0.373)	-7.423
226-96i-64g-48e	New	14.601	(0.500,-0.638,-0.421)	(0.583,-0.583,-0.583)	(0.500,-0.298,-0.500)	-6.660
225-96k-96k-32f	New	13.221	(0.319,-0.319, 0.449)	(0.377,-0.623, 0.744)	(0.337,-0.163, 0.337)	-7.076
225-192l-192l-192l	New	18.868	(-0.383, 0.331,-0.278)	(-0.431, 0.336,-0.215)	(-0.592, 0.464,-0.792)	-7.363
225-192l-192l-96j	New	20.015	(-0.376, 0.276, 0.327)	(-0.434, 0.231,-0.317)	(-0.316, 0.267, 0.500)	-7.098
224-48l-48l-24l	D144-D8	11.814	(0.631, 0.546, 0.715)	(0.450, 0.634, 0.794)	(0.833, 0.417, 0.745)	-7.422
224-24k-24k-24k	D72-D7	8.757	(0.291, 0.711, 0.103)	(0.254, 0.057, 0.057)	(0.011, 0.215, 0.215)	-7.124
224-24h-24k-24k	D72-D8	10.214	(0.000, 0.821, 0.500)	(0.116, 0.116, 0.447)	(0.810, 0.359, 0.810)	-7.545
224-48l-48l-24j	New	10.245	(0.648, 0.855, 0.947)	(0.053, 0.751, 0.849)	(0.952, 0.548, 0.750)	-7.212
223-48l-24k-12h	New	9.742	(0.308, 0.692, 0.869)	(0.361, 0.634, 0.007)	(0.431, 0.500, 0.000)	-7.115
221-24m-24l-8g	P56-P8	8.658	(0.639, 0.639, 0.161)	(0.081, 0.500, 0.694)	(0.696, 0.304, 0.304)	-7.170
221-48n-48n-24k	P120-P8	11.971	(0.442, 0.279, 0.103)	(0.370, 0.287, 0.203)	(0.386, 0.301, 0.000)	-7.541
221-48n-48n-24l	P120-P8	11.887	(0.704, 0.787, 0.871)	(0.778, 0.603, 0.941)	(0.885, 0.500, 0.799)	-7.499
217-48h-48h-48h	G72-G8	11.982	(0.512,-0.132, 0.796)	(0.094, 0.248, 0.603)	(0.163, 0.244, 0.684)	-7.599
217-48h-48h-48h	6*A6 ³ 12 ³	11.168	(0.491,-0.294,-0.141)	(0.431,-0.342,-0.252)	(0.411,-0.192,-0.099)	-7.215
217-48h-48h-24g	6A6	10.504	(-0.013,-0.179,-0.366)	(-0.099,-0.292,-0.387)	(0.049,-0.347, 0.049)	-7.404
216-96e-48h-16e	New	11.314	(0.293, 0.530,-0.618)	(0.415, 0.585,-0.239)	(0.858, 0.641,-0.641)	-7.228
216-96e-96e-48h	New	13.869	(0.319,-0.608,-0.463)	(0.251,-0.615,-0.545)	(0.443,-0.285,-0.215)	-7.383
215-24j-12i-4e	New	7.589	(0.085, 0.448, 0.319)	(0.533, 0.765, 0.765)	(0.698, 0.302, 0.302)	-7.038
215-24j-24j-24j	6*A6 ³ 12 ³	11.081	(0.636, 0.725, 0.545)	(0.167, 0.466, 0.377)	(0.054, 0.368, 0.534)	-6.996
215-24j-24j-24j	6*A6 ³ 8 ³	9.231	(0.654, 0.763, 0.549)	(0.069, 0.175, 0.459)	(0.129, 0.429, 0.326)	-7.238
214-48i-48i-48i	G72-G8	12.568	(-0.121,-0.187, 0.721)	(-0.033,-0.629, 0.536)	(-0.029,-0.121, 0.696)	-7.263
212-12d-8c-4a	New	5.964	(0.295, 0.955, 0.125)	(0.751, 0.751,-0.249)	(0.125, 0.125, 0.125)	-7.055
212-24e-24e-8c	New	10.254	(0.813, 0.518, 0.313)	(0.728, 0.563, 0.706)	(0.702, 0.702, 0.702)	-6.485
207-24k-24k-8g	P56-P7	8.554	(0.958, 0.574, 0.317)	(0.805, 0.426, 0.735)	(0.706, 0.706, 0.706)	-7.299
206-48e-48e-48e	6*A7 ⁶	11.577	(0.156, 0.241,-0.669)	(0.790, 0.125, 0.050)	(0.901, 0.065, 0.030)	-7.466
206-48e-48e-48e	6*A6 ⁶	11.826	(0.085, 0.009, 0.814)	(0.068, 0.128, 0.851)	(0.156, 0.195, 0.795)	-7.347
206-48e-48e-48e	6*Z6 ⁶	10.526	(-0.028,-0.402, 0.093)	(-0.101,-0.361, 0.214)	(-0.237,-0.296, 0.434)	-6.985
204-48h-48h-24g	New	10.860	(-0.162,-0.216, 0.344)	(-0.103,-0.568, 0.353)	(0.561, 0.000, 0.395)	-7.062
203-96g-96g-32e	FCC-(C ₂₈) ₂ [23]	15.028	(0.393, 0.552, 0.823)	(0.143, 0.451, 0.511)	(0.575, 0.925, 0.575)	-7.095
201-24h-24h-8e	D56-D7	7.598	(0.787, 0.105, 0.649)	(0.280, 0.903, 0.018)	(0.147, 0.853, 0.147)	-7.044
200-12k-8i-6h	New	7.272	(0.500, 0.777, 0.345)	(0.666, 0.666, 0.666)	(0.500, 0.091, 0.500)	-6.979
200-24l-12j-8i	New	7.552	(0.165, 0.811, 0.591)	(0.000, 0.090, 0.654)	(0.725, 0.725, 0.725)	-6.821
200-12k-8i-6f	New	6.682	(-0.305, 0.800, 0.500)	(-0.400, 1.000, 0.500)	(-0.317, 0.317, 0.317)	-6.952
200-12j-8i-6g	New	6.247	(0.279, 0.291, 0.000)	(0.390, 0.500, 0.000)	(0.195, 0.805, 0.805)	-6.642
197-24f-24f-8c	P56-P7[16, 25]	8.359	(-0.098,-0.686, 0.297)	(0.247,-0.419,-0.026)	(0.236,-0.236, 0.236)	-7.183
195-12j-12j-6g	New	6.513	(0.952, 0.669, 0.271)	(0.856, 0.618, 0.066)	(0.000, 0.500, 0.389)	-6.845

230-96h-96h-96h (G144-G8) and P type 229-96l-48k-48k (P192-P8, proposed before[17, 19]). Most of them are never mentioned in literatures. Their corresponding lattice constants and inequivalent positions are summa-

rized in Table II and their corresponding perspective crystalline views can be found in the supplementary Fig S3 and Fig S4. Some of them are identified to be the previously proposed FCC-(C₃₆)₂[23] (227-96g-96g-96g),

FCC-(C₄₀)₂[23] (227-192i-96g-32e), FCC-(C₂₈)₂[23] (203-96g-96g-32e) and P56-P7[16, 25] (195-12j-12j-6g). We notice that many new surface structures, such as 227-192i-192i-96g (D120-D7), 227-192i-192i-192i (D144-D8), 224-48l-48l-24l (D144-D8), 221-24m-24l-8g (P56-P8), 221-48n-48n-24k (P120-P8), 217-48h-48h-48h (G72-G8), and 201-24h-24h-8e (D56-D7) have not been proposed previously. Some new structures belonging to the same space and with the same atomic positions have the same name (see 217-48h-48h-48h, 215-24j-24j-24j and 206-48e-48e-48e) and we provide additional signs reflecting their structural characters for distinguishing them. For example, 6*A⁷⁶ means the structure with characteristic hexagons connecting six heptagons at its six armchair edges and 6*Z⁶⁶ indicates characteristic hexagons connecting six hexagons at its six zigzag vertexes.

From table II, we can see that these C-sp²-TDTCNs distribute in space groups of 230, 229, 228, 227, 226, 225, 224, 223, 221, 217, 216, 215, 214, 212, 207, 206, 204, 203, 201, 200, 197 and 195. This does not mean that C-sp²-TDTCNs can not be found in other space groups. For example, we found 227-96g-96g-32e in No.210 as 210-96h-96h-32e with relatively lower symmetry. In addition, we have also found some C-sp²-TDTCNs with three inequivalent atomic positions degenerating to those with one or two inequivalent atomic positions. Such as 213-8c-4a-4b to 230-16b (IK4) and 220-48e-48e-48e to 230-96h-48g. More examples can be found in Table SIII in the supplementary information.

Additional discussions

All the post-processes of structure optimizations for these C-sp²-TDTCNs are performed with density functional theory (DFT) based first-principles method by regarding these C-sp²-TDTCNs as sp²-hybridized carbon crystals with calculation details provided in the supplementary information. We should point out that, after the optimization, a few C-sp²-TDTCNs do not satisfy the requirements of C-sp²-TDTCNs in bond angles, bond lengths or neighbours, which are understandable and acceptable. We have also considered energy evaluation of these sp²-hybridized carbon crystals but have not performed systematic investigation on the dynamical stability due to the large computational cost. Our results show that some of them are energetically viable, such as 230-96h-96h-96h (G144-G8), 229-96l-48k-48k (P192-P8), 227-192i-192i-96g (D120-D7), 224-24h-24k-24k (D72-D8), 221-48n-48n-24k (P120-P8), 217-48h-48h-48h (G72-G8), 221-48n-24k (P72-P8), 221-48n-24l (P72-P8), 204-48h-24g (G36-G7), and 224-24i (6.8²D) which possess remarkable energetic stability comparable to that of diamond (-7.623 eV/atom). Most of them are more sta-

ble than the experimentally produced graphdiyne (-7.06 eV/atom). In addition, we want to point out that some of them may be dynamically unstable like K4-carbon (214-16b) [37], and some of them such as sp²-diamond and 6.8²D have been confirmed dynamically stable[56].

CONCLUSION

Based on a simple restriction of lattice in cubic and inequivalent atomic positions not exceeding three, we have introduced a simple method for systematic searching of C-sp²-TDTCNs in all the cubic space groups from No.195 to No.230 and found many topological intriguing C-sp²-TDTCNs. These C-sp²-TDTCNs are named according to their space group numbers and Wyckoff positions, which can provide fundamental crystallographic information for excluding future repeating structures. All of these C-sp²-TDTCNs can be considered as good templates for searching for carbon crystals with novel properties, predicting high pressure phases of element nitrogen and designing TD hydrocarbon crystals. We believe that our results are of wide interests in both mathematics and crystallography.

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- [57] These structures, as carbon crystals, are three- and four-connected after optimization. We provide the final cohesive energies and their initial configurations.

SUPPLEMENTARY INFORMATION for "Systematic enumeration of crystalline networks with only sp^2 configuration in cubic lattices"

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We optimized these C- sp^2 -TDTCNs through regarding them as carbon crystals. Both the lattice constant and atomic positions of these C- sp^2 -TDTCNs were fully optimized until the residual forces on each carbon atom to be less than 0.02 eV/Å. All the calculations of structure optimizations and energetic stability evaluations were performed using the density functional theory based VASP code [1] with the projected augmented wave (PAW) potential [2]. The exchange and correlation are approximated by general gradient approximation (GGA) developed by Perdew et al. [3]. The wave functions for all systems are expanded by plane-wave functions with cutoff energy of 500 eV. The Brillouin zone sample meshes based on the Monkhorst-Pack scheme are set to be denser enough (less than 0.25 1/Å) to ensure the accuracy of our calculations.

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TABLE I: The nominations, relations, lattice constant (LC:Å), inequivalent positions (POS), and cohesive energy (Ecoh: eV/atom) of C-sp²-TDTCNs with only one inequivalent atomic position

C-TDTCNs	Relation	LC	POS	Ecoh
230-96h	6.8 ² G	9.587	(0.117, 0.548, 0.424)	-7.391
230-16b	IK4-carbon	4.426	(-0.125,-0.375, 0.375)	-6.346
229-48k	6.8 ² P	7.843	(0.689, 0.689, 0.913)	-7.364
227-96g	sp ² -diamond	9.667	(-0.049, 0.549,-0.726)	-7.179
224-24i	6.8 ² D	6.095	(0.250, 0.087, 0.589)	-7.585
214-8a	K4-carbon	4.126	(-0.125,-0.375, 0.375)	-6.529
206-48e	3/6/c5	7.505	(0.345,-0.111, 0.015)	-6.798
228-192h	6.8 ² D	12.191	(0.207, 0.043, 0.875)	-7.585
227-192i	6.8 ² D	12.191	(0.625, 0.793, 0.543)	-7.585
223-48l	6.8 ² P	7.843	(0.311, 0.087, 0.689)	-7.364
222-48i	6.8 ² P	7.843	(0.311, 0.087, 0.689)	-7.364
220-16c	IK4-carbon	4.426	(-0.125,-0.375, 0.375)	-6.346
215-24j	6.8 ² D	6.095	(0.250, 0.087, 0.589)	-7.585
213-8c	K4-carbon	4.126	(-0.125,-0.375, 0.375)	-6.529
212-8c	K4-carbon	4.126	(0.375, 0.375, 0.375)	-6.529
211-48j	6.8 ² P	7.843	(0.689, 0.689, 0.913)	-7.364
210-96h	sp ² -diamond	9.667	(-0.049, 0.549,-0.726)	-7.179
206-16c	IK4-carbon	4.426	(-0.125,-0.375, 0.375)	-6.346
204-48h	6.8 ² P	7.843	(0.689, 0.689, 0.913)	-7.364
203-96g	sp ² -diamond	9.667	(-0.049, 0.549,-0.726)	-7.179
201-24h	6.8 ² D	6.095	(0.250, 0.087, 0.589)	-7.585
199-8a	K4-carbon	4.126	(-0.125,-0.375, 0.375)	-6.529

TABLE II: The nominations, relations, lattice constant (LC:Å), inequivalent positions (POS), and cohesive energy (Ecoh: eV/atom) of C-sp²-TDTCNs with two inequivalent atomic positions

C-TDTCNs	Relation	LC	POS1	POS2	Ecoh
228-192h-192h	6.8 ² P	15.685	(0.043, 0.155, 0.845)	(0.043, 0.155, 0.655)	-7.364
228-96g-96g	6.8 ² D	12.191	(0.875, 0.289, 0.539)	(0.291, 0.375, 0.041)	-7.585
227-96h-96h	6.8 ² D	12.191	(0.467,-0.375, 0.783)	(0.462, 0.712, 0.375)	-7.585
226-192j-192j	6.8 ² P	15.685	(0.155, 0.957, 0.845)	(0.207, 0.905, 0.905)	-7.364
221-24m-24m	6.8 ² P	7.843	(0.311, 0.087, 0.689)	(0.413, 0.189, 0.811)	-7.364
220-48e-48e	6.8 ² G	9.587	(-0.798,-0.363,-0.674)	(-0.617,-0.547,-0.076)	-7.391
219-96h-96h	6.8 ² D	12.191	(0.125, 0.043, 0.793)	(0.207, 0.043, 0.875)	-7.585
219-48g-32e	215-6g-4e	9.808	(0.250, 0.070, 0.750)	(0.154, 0.154, 0.846)	-6.365
218-24i-24i	6.8 ² P	7.843	(0.087,-0.311, 0.311)	(-0.087,-0.311, 0.311)	-7.364
218-12f-8e	217-12e-8c	4.979	(0.648, 0.000, 0.000)	(0.324,-0.324,-0.324)	-6.249
217-24g-24g	6.8 ² P	7.843	(0.087,-0.311, 0.311)	(-0.087,-0.311, 0.311)	-7.364
216-48h-48h	sp ² -diamond	9.667	(-0.049, 0.549,-0.726)	(-0.201, 0.476,-0.299)	-7.179
216-96i-96i	6.8 ² D	12.191	(0.043, 0.125, 0.293)	(0.043, 0.125, 0.793)	-7.585
214-8a-8b	IK4-carbn	4.426	(-0.125,-0.375, 0.375)	(0.125,-0.625, 0.625)	-6.346
214-48i-48i	6.8 ² G	9.598	(0.452, 0.424, 0.617)	(0.576, 0.383, 0.548)	-7.391
213-4a-4b	K4-carbon	4.126	(0.625, 0.625, 0.625)	(0.125,-0.625, 0.625)	-6.529
212-4a-4b	K4-carbon	4.126	(0.875, 0.625, 0.375)	(0.625, 0.625, 0.625)	-6.529
210-96h-32e	227-96h-32e	11.203	(0.834,-0.166, 0.506)	(0.387, 0.613, 0.613)	-7.191
209-48h-32f	C20	9.146	(-0.139,-0.139, 0.139)	(0.000, -0.198,0.198)	-6.878
209-48i-32f	225-48g-32f	9.572	(0.250, 0.430,-0.250)	(0.850, 0.650,-0.650)	-6.819
208-24m-24m	6.8 ² P	7.843	(0.087,-0.311, 0.311)	(0.587,-0.189, 0.189)	-7.364
208-12l-12l	6.8 ² D	6.095	(0.250, 0.913, 0.413)	(0.250, 0.587, 0.087)	-7.585
207-24k-24k	6.8 ² P	7.843	(0.087,-0.311, 0.311)	(0.587,-0.189, 0.189)	-7.364
205-8c-8c	IK4-carbon	4.426	(-0.125,-0.375, 0.375)	(-0.125,-0.625, 0.125)	-6.346
205-24d-24d	206-48e	7.505	(0.595, 0.235,-0.361)	(0.095, 0.735, 0.139)	-6.798
203-96g-32e	227-96g-32e	11.203	(0.834,-0.166, 0.506)	(0.387, 0.613, 0.613)	-7.191
202-48h-32f	C20	9.146	(-0.139,-0.139, 0.139)	(0.000, -0.198,0.198)	-6.878
202-48g-32f	225-48g-32f	9.572	(0.250, 0.430,-0.250)	(0.850, 0.650,-0.650)	-6.819
201-24h-24h	6.8 ² P	7.843	(0.087,-0.311, 0.311)	(0.587,-0.189, 0.189)	-7.364
201-12f-8e	224-12g-8e	5.342	(0.000, 0.000, 0.362)	(0.358, 0.642, 0.642)	-6.721
198-4a-4b	K4-carbon	4.126	(0.875, 0.625, 0.375)	(0.625, 0.625, 0.625)	-6.529
197-24g-24g	6.8 ² P	7.843	(0.087,-0.311, 0.311)	(-0.087,-0.311, 0.311)	-7.364
197-12e-8c	Cage10-N	4.979	(0.648, 0.000, 0.000)	(0.324,-0.324,-0.324)	-6.249
196-48h-48h	sp ² -diamond	9.667	(-0.049, 0.549,-0.726)	(-0.201, 0.476,-0.299)	-7.179
195-12j-12j	6.8 ² D	6.095	(0.250, 0.913, 0.413)	(0.250, 0.587, 0.087)	-7.585

TABLE III: Nominations, relations, Lattice constant (LC:Å), Inequivalent positions (POS), Cohesive energy (Ecoh: eV/atom) of C-sp²-TDTCNs with only one inequivalent atomic position

C-TDTCNs	Relation	LC	POS1	POS2	POS3	Ecoh
228-192h-192h-192h	224-24h-24k-24k	20.233	(-0.343, 0.845, 0.577)	(0.440, 0.784, 0.940)	(0.501, 0.750, 0.910)	-7.545
226-192j-192j-192j	221-48n-24l	18.927	(0.420, 0.315, 0.867)	(0.464, 0.250, 0.863)	(0.367, 0.314, 0.920)	-7.525
220-48e-48e-48e	230-96h-48g	10.340	(-0.144,-0.326, 0.776)	(-0.301,-0.875, 0.551)	(0.394,-0.526, 0.576)	-6.824
216-48h-16e-16e	C20	9.125	(0.547, 0.453, 0.272)	(0.373, 0.127, 0.627)	(0.610, 0.390, 0.390)	-6.878
213-8c-4a-4b	IK4-carbon	4.426	(-0.125,-0.375, 0.375)	(0.375, 0.375, 0.375)	(0.125,-0.625, 0.625)	-6.346
212-8c-4a-4b	IK4-carbon	4.426	(0.125,-0.625, 0.625)	(-0.125,-0.375, 0.375)	(-0.125,-0.625, 0.125)	-6.346
210-96h-96h-32e	227-96g-96g-32e	12.652	(0.169,-0.533, 0.830)	(0.068,-0.288, 0.788)	(0.171,-0.171, 0.671)	-7.207
210-96h-96h-96h	227-96g-96g-96g	17.491	(-0.105, 0.605, 0.801)	(-0.244, 0.858, 0.858)	(-0.123, 0.778, 0.778)	-7.125
209-96j-96j-96j	225-192l-96k	15.146	(0.596,-0.839,-0.728)	(0.455,-0.307,-0.307)	(0.404,-0.161,-0.272)	-7.219
209-96j-96j-32f	225-96k-96k-32f	13.221	(0.319,-0.319, 0.449)	(0.377,-0.623, 0.744)	(0.337,-0.163, 0.337)	-7.076
207-24k-24k-24k	221-48n-24k	9.462	(0.340, 0.234, 0.129)	(0.000, 0.572, 0.774)	(0.660, 0.766, 0.871)	-7.521
205-24k-24k-24k	221-48n-24k	9.462	(0.340, 0.234, 0.129)	(0.000, 0.572, 0.774)	(0.660, 0.766, 0.871)	-7.521
203-96g-96g-32e	227-96g-96g-32e	12.652	(0.169, 0.967, 0.330)	(0.213, 0.713, 0.932)	(0.171, 0.829, 0.671)	-7.207
203-96g-96g-96g	227-96g-96g-96g	17.491	(-0.105, 0.605, 0.801)	(-0.244, 0.858, 0.858)	(-0.123, 0.778, 0.778)	-7.125
202-96j-96j-96j	225-192l-96k	15.146	(0.596,-0.839,-0.728)	(0.455,-0.307,-0.307)	(0.339,-0.096,-0.272)	-7.219
202-96i-96i-32f	225-96k-96k-32f	13.221	(0.319,-0.319, 0.449)	(0.377,-0.623, 0.744)	(0.337,-0.163, 0.337)	-7.076
202-96i-32f-32f	200-12j-8f	10.901	(0.250, 0.864, 0.932)	(0.364, 0.864, 0.864)	(0.135, 0.864, 0.864)	-7.067
201-24h-24h-24h	204-48h-24g	9.365	(0.500, 0.928, 0.785)	(0.726, 0.867, 0.658)	(0.367, 0.842, 0.774)	-7.517
197-24f-24f-24f	204-48h-24g	9.365	(0.500, 0.928, 0.785)	(0.367, 0.842, 0.774)	(0.342, 0.726, 0.867)	-7.517
195-12j-4e-4e	200-12j-8f	5.412	(0.499, 0.271,-0.891)	(0.718, 0.718,-0.282)	(0.285,-0.285,-0.715)	-7.067

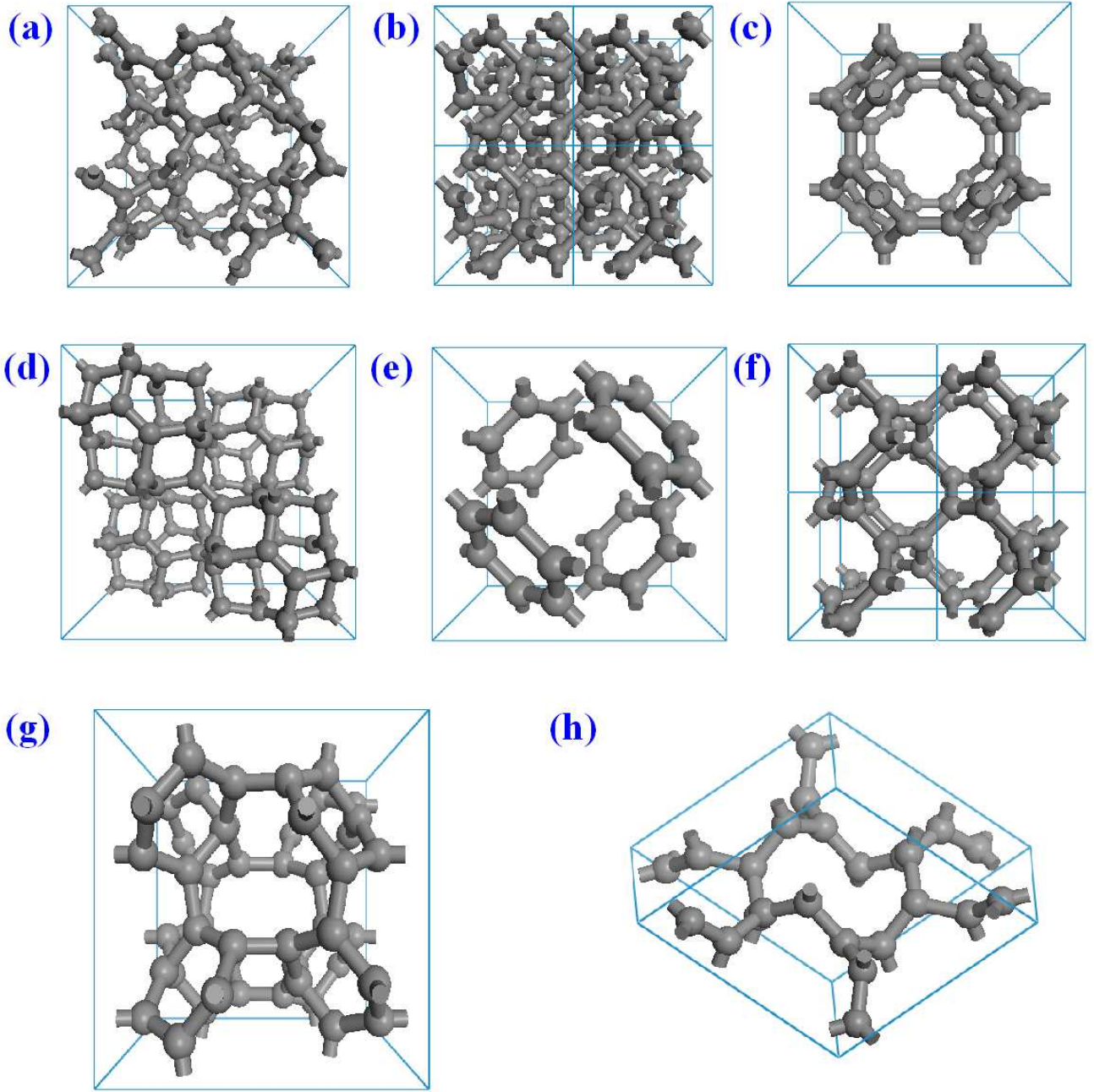


FIG. 1: Crystalline views of the seven inequivalent C-sp²-TDTCNs. (a), (b), (c), (d), (e) and (f) are 230-96h (6.8²G), 230-16b (IK4), 229-48k (6.8²P), 227-96g (sp²-diamond), 224-24i (6.8²D) and 214-8a (K4), respectively. (g) and (h) are the crystalline views of 206-48e (3/6/c5) in crystal cell and primitive cell, respectively.

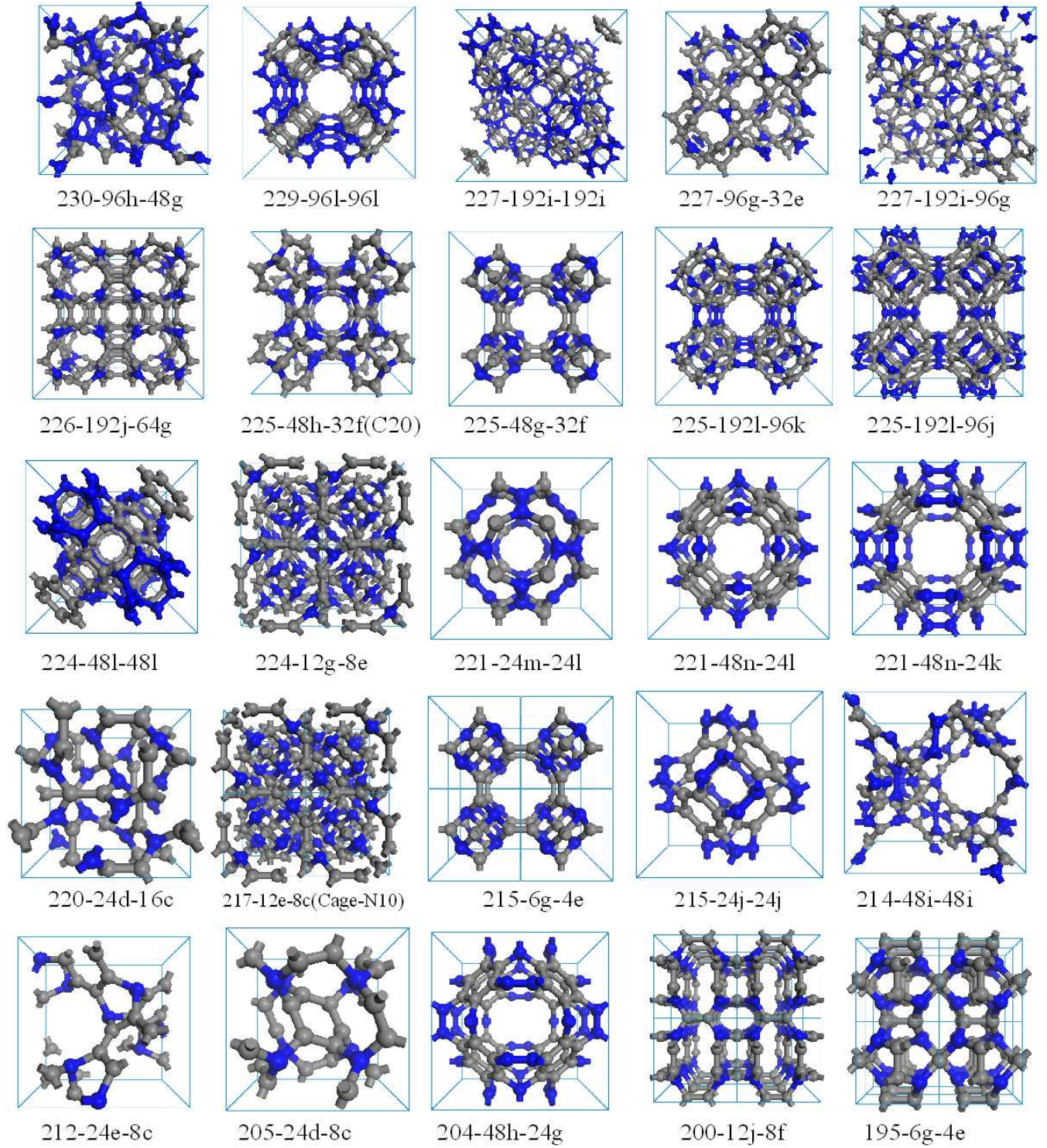


FIG. 2: Crystalline views of the 25 inequivalent C-sp²-TDTCNs with three inequivalent positions, where different atomic positions are shown in different colors

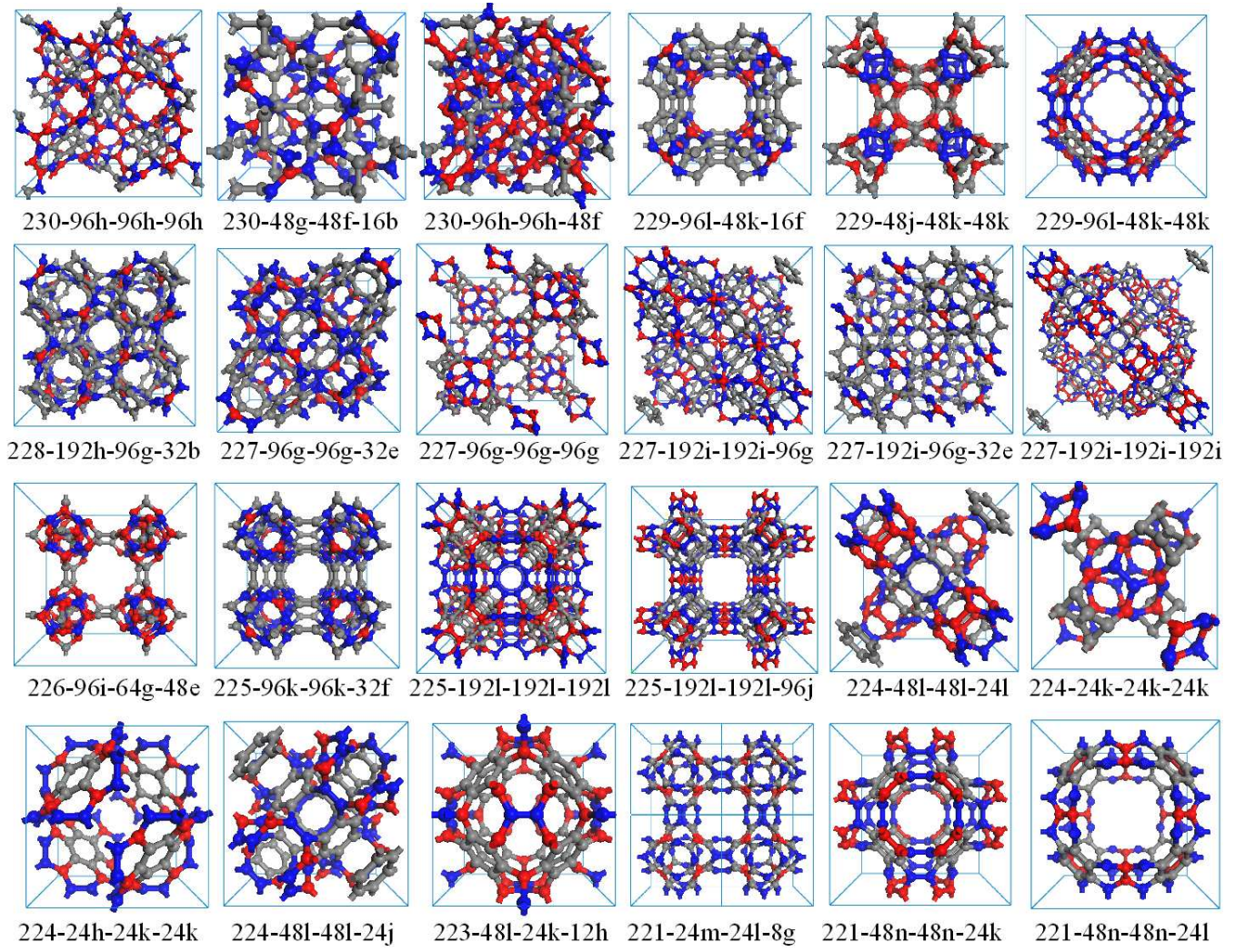


FIG. 3: Crystalline views of the 24 inequivalent C-sp²-TDTCNs (No.230-221) with three inequivalent positions, where different atomic positions are shown in different colors.

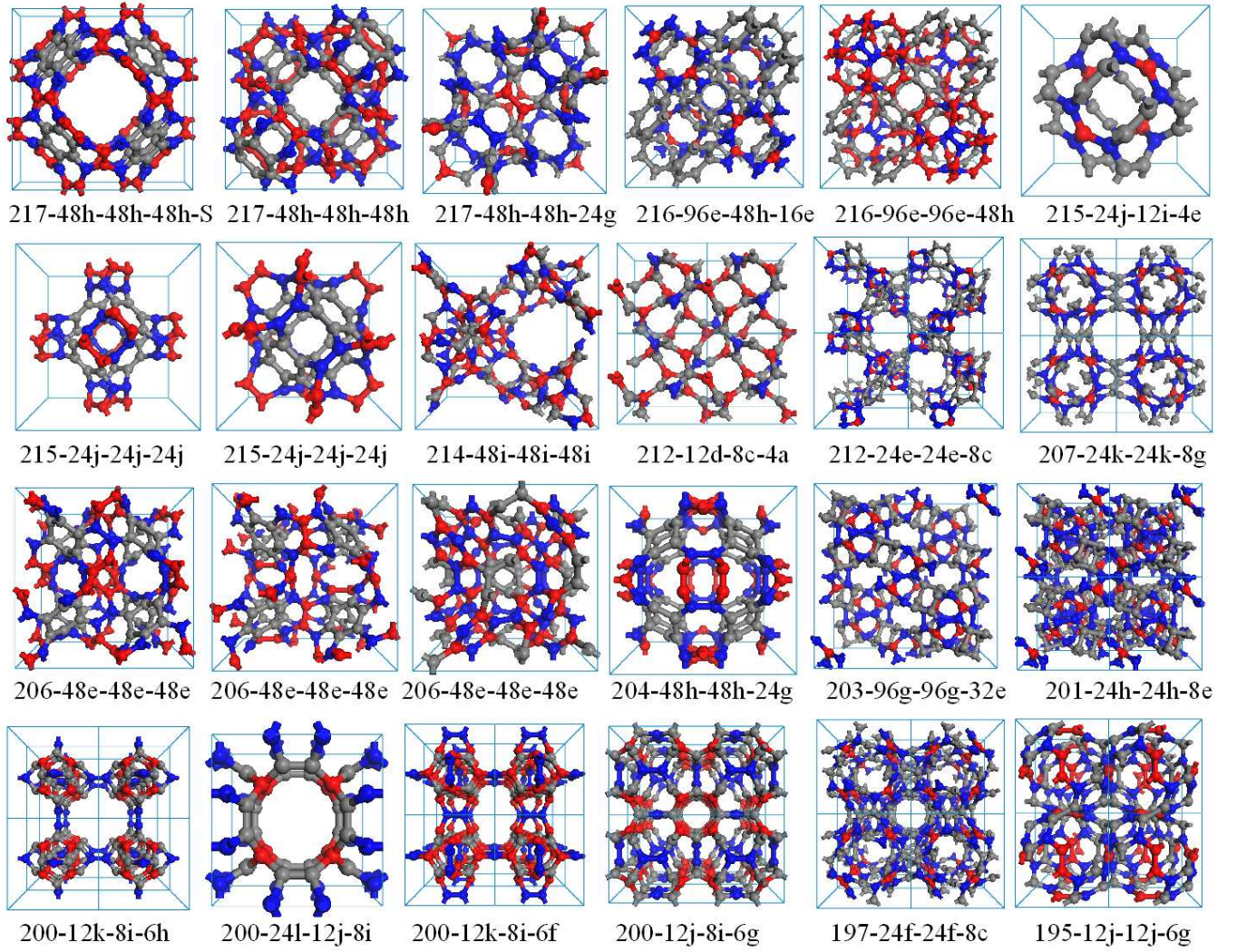


FIG. 4: Crystalline views of the 24 inequivalent C-sp²-TDTCNs (No.216-195) with three inequivalent positions, where different atomic positions are shown in different colors.